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High-temperature Raman spectroscopy study of the amorphous-to-crystalline transition in zirconium tungstate

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Abstract – *In situ* Raman spectroscopic measurements of amorphous zirconium tungstate were performed at different temperatures to clarify some issues related to the amorphous-to-crystalline phase transition. According to the results, at temperatures higher than 600 °C amorphous zirconium tungstate recrystallizes to the β-ZrW_2O_8 phase before converting to α-ZrW_2O_8 upon cooling to room temperature.

The crystal structure of zirconium tungstate at room conditions (α-ZrW_2O_8) is usually described as an open three-dimensional network of corner-sharing ZrO_6 and WO_4 units, in which one of the four corners of each WO_4 tetrahedra is not shared. The high degree of flexibility of such framework gives place to an anomalous isotropic negative thermal expansion over a wide range of temperatures, as also to several phase transitions at high temperatures and/or pressures. Around 155°C, α-ZrW_2O_8 undergoes an order-disorder phase transition to β-ZrW_2O_8. At pressures above 0.2 GPa and room temperature, zirconium tungstate exhibits another structural phase transition, to orthorhombic γ-ZrW_2O_8. This compound undergoes pressure-induced amorphization (PIA) at relatively low pressures, starting at 1.5 to 2 GPa. PIA in zirconium tungstate is irreversible upon pressure release, and the amorphous phase (a-ZrW_2O_8) only recrystallizes when heated above 600°C. Noteworthy, the amorphous-to-crystalline phase transition in zirconium tungstate is endothermic, *i.e.*, it proceeds with increase of entropy. In this work, we have performed Raman spectroscopy of samples of amorphous ZrW_2O_8 *in situ*, at high temperatures, aiming to clarify some details of the endothermic recrystallization of zirconium tungstate.

The sample of amorphous zirconium tungstate was prepared by pressing pellets of α-ZrW_2O_8 to 7.7GPa at room temperature in a toroidal high-pressure chamber. Raman spectra were obtained using a home-built Raman microprobe. The sample was heated using a home-built apparatus basically consisting of a platinum heating wire and a electrical power controller. The temperature measurement system used a K-type thermocouple and was checked using the orthorhombic → tetragonal phase transition of WO_3.

Figures 1 and 2 show representative Raman spectra taken during the temperature increasing up to 617°C and during the cooling down the room temperature. Despite the similarity between the local structures of the amorphous phase and γ-ZrW_2O_8, no sign of the latter could be found on the Raman spectra taken during recrystallization. The results demonstrate that amorphous-ZrW_2O_8 recrystallizes at room pressure to the β-ZrW_2O_8 phase. This phase, upon cooling, suffers a phase transition to α-ZrW_2O_8, the more ordered phase stable at room conditions.

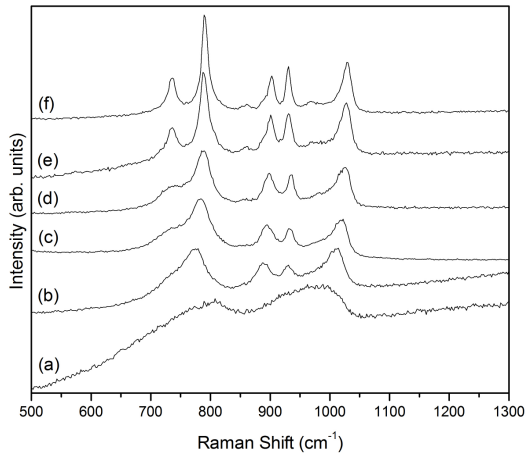

Figure 1: Raman spectra of zirconium tungstate. (a) Amorphous sample after pressure treatment at 7.7 GPa and room temperature. (b) The same sample after heating to 617°C during 34 min. Spectra taken during the cooling at (c) 350°C, (d) 182°C, (e) 94°C, and (f) room temperature.

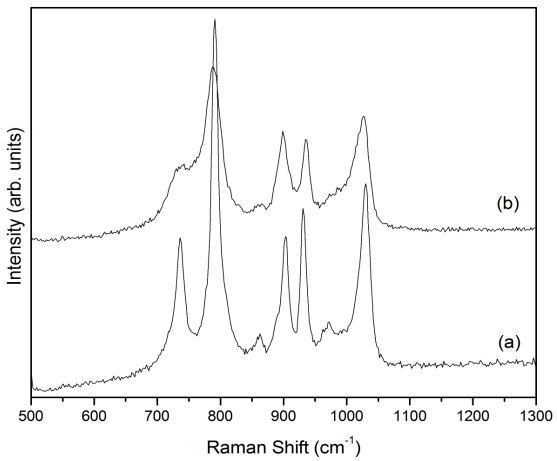

Figure 2: Comparison between the Raman spectra of (a) α-ZrW_2O_8 at ambient temperature, and (b) β-ZrW_2O_8 at 177°C.